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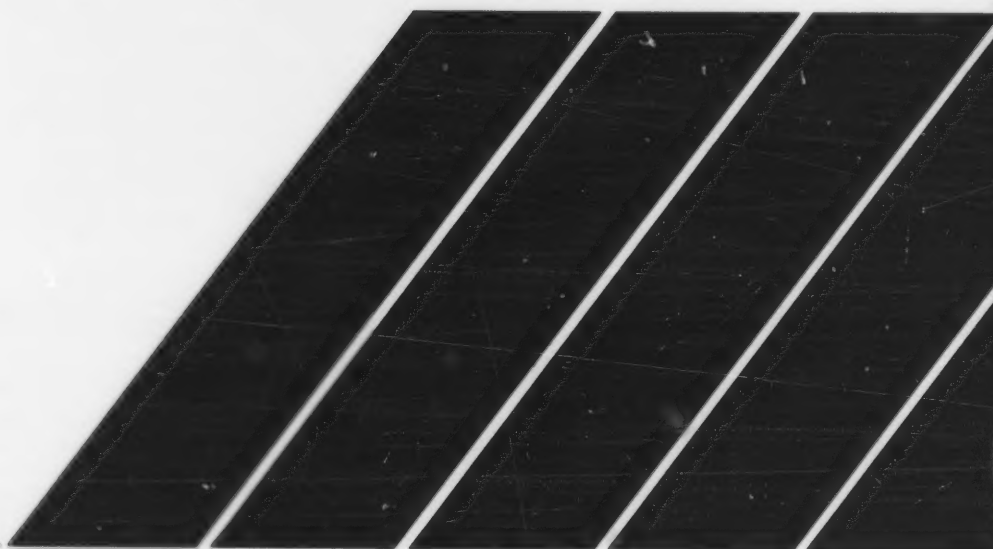
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TECHNICAL AND ENVIRONMENTAL ASSESSMENT OF THE SCRAP TIRE VACUUM PYROLYSIS PROCESS



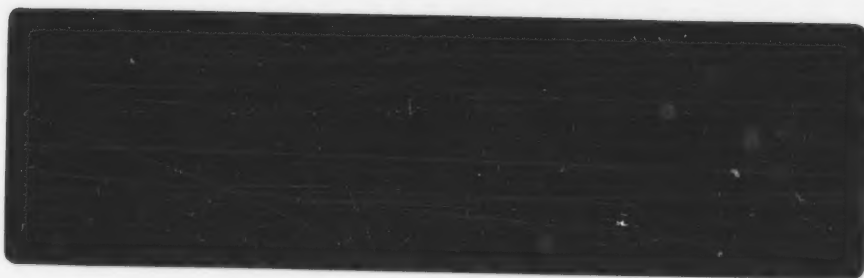
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**TECHNICAL AND ENVIRONMENTAL ASSESSMENT
OF THE SCRAP TIRE VACUUM PYROLYSIS PROCESS**

PREPARED FOR:

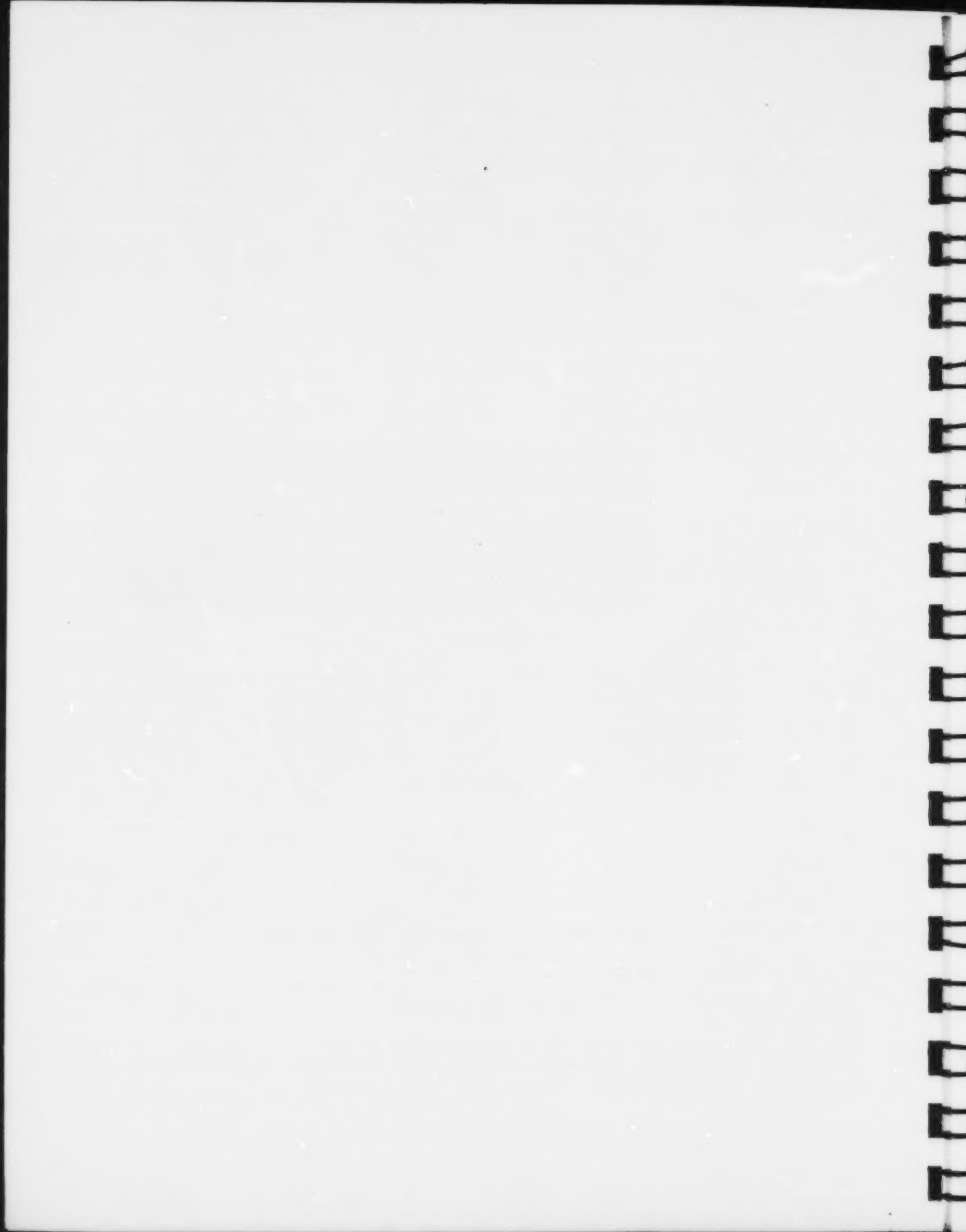
Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
Ottawa, Ont.
DSS Contract No. 045SZ.23341-9-4025
November, 1990

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SCIENTIFIC AUTHORITY:

49 pp
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CITATION

Roy, C., B. de Caumia, B. Lebreque, D. Blanchette, H. Pakdel, and V. Roy, Carbovac Research Inc. Technical and Environmental Assessment of the Scrap Tire Vacuum Pyrolysis Process. DSS Contract No. 045SZ.23341-9-4025. Efficiency and Alternative Energy Technology Branch, Energy, Mines and Resources Canada, Ottawa, Ontario. 1990 (49 pp.)

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NOTE

Funding for this project was provided by the Federal Panel on Energy Research and Development, Energy, Mines and Resources Canada.

ACKNOWLEDGEMENTS

The following individuals are gratefully acknowledged for their participation in this work: Mr. Jean-Marc Roy; Mr. Frédéric Charest; Mrs. Geneviève Couture; Mrs. C. Lacroix; Mrs. Hélène Aubin and Mrs. Nathalie Auclair. The technical contribution of Mr. Steve Menegoz has been appreciated.



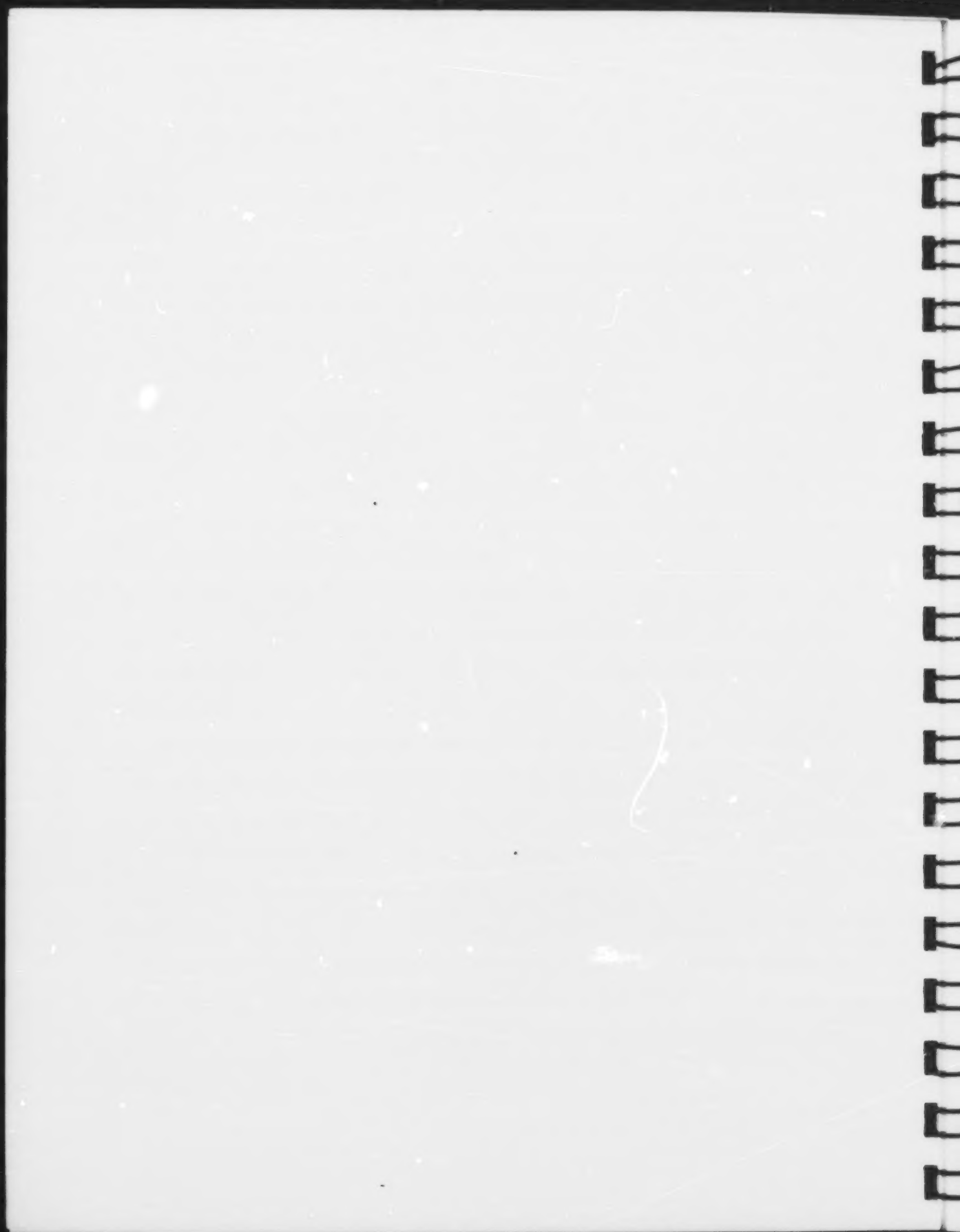
TABLE OF CONTENTS

ABSTRACT	6
RÉSUMÉ	7
INTRODUCTION	9
VACUUM PYROLYSIS PROCESS	11
BACKGROUND	11
PROCESS DEVELOPMENT UNIT STUDY	13
PILOT PLANT STUDY	14
OIL AND CARBON BLACK ANALYSIS	15
PROCESS FEASIBILITY	18
ENVIRONMENTAL ASPECTS	21
FIGURES AND PHOTOGRAPH	23-28
REFERENCES	29
APPENDIX A: VALUABLE CHEMICALS FOUND IN THE PYROLYSIS OIL	
APPENDIX B: MICROTOX TESTING OF THE AQUEOUS PHASE	



ABSTRACT

Tire recycling has become a necessity because of the huge piles of tires which represent a threat to the environment. There is about one worn tire produced per year and per person in the developed countries. The used tires represent a source of energy and valuable chemical products. By thermal decomposition of rubber under reduced pressure, it is possible to recover the useful compounds. A step by step approach has been used, from bench scale batch systems, to process development unit and finally pilot plant, to experiment and develop vacuum pyrolysis of used tires. Yields are: 55% oil, 25% carbon black, 9% steel, 5% fiber and 6% gas. The maximum recovery of oil was performed at 415°C below 2 kPa abs. The specific gravity of this oil was 0.95, its gross heating value was 43 MJ/kg and total sulfur content about 0.8%. It was rich in limonene, benzol and other petrochemical components. The carbon black favorably compared with the low standard grades and may find an application in low grade rubber goods following further research and development. From an environmental point of view, the quality of the gas emissions was found to be acceptable based on the Province of Quebec regulations. The aqueous phase contains toxic substances which will be eliminated after blending and burning it with pyrolysis oils used to heat up the reactor. The heat of pyrolysis for the reactions is low, estimated around 700 kJ/kg. The process has been tested in a 200 kg/h pilot plant, which positively demonstrated the possibility of continuously feeding large chunks of rubber under a vacuum. The process feasibility is promising, with returns on the investment of 31% after three years of operation.



RESUME

Le recyclage des pneus est devenu une nécessité en raison de l'importance grandissante des dépôts de pneus, lesquels constituent une menace pour l'environnement. Dans les pays industrialisés, on génère environ un pneu usé par personne par année. Les pneus usés sont une source d'énergie et de produits chimiques valables commercialement. Par la décomposition thermique du caoutchouc sous pression réduite, il est possible de récupérer des composés utiles. Une approche par étapes a été effectuée, à partir d'unités d'essais de laboratoire en discontinu, d'une unité de développement de procédé et finalement à l'échelle pilote, pour expérimenter et développer la pyrolyse sous vide des pneus usés. Les rendements sont: 55% d'huile, 28% de noir de carbone, 9% d'acier, 5% de fibres et 6% de gaz.

Le rendement maximal en huile a été obtenu pour une température de 415°C sous une pression absolue de 2 kPa. La densité de cette huile est 0.95, son pouvoir calorifique supérieur 43 MJ/kg, et la teneur en soufre d'environ 0.8%. Cette huile est riche en limonène, benzol et autres composés pétrochimiques. Le noir de carbone se compare bien avec les noirs de carbone commerciaux de grades inférieurs et pourrait être réutilisé pour la fabrication de certaines pièces en caoutchouc, moyennant d'autres travaux de R et D.

Du point de vue environnemental, la qualité des émissions gazeuses est acceptable d'après les règlements en vigueur dans la province de Québec. La phase aqueuse contient des substances toxiques, lesquelles pourront être éliminées après mélange et combustion avec une partie de l'huile pyrolytique qui servira à chauffer le réacteur. La chaleur requise pour les réactions de pyrolyse est faible, étant

estimée à environ 700 kJ/kg. Le procédé a été expérimenté à l'échelle d'une usine pilote de 200 kg/h, et la possibilité d'alimenter en continu sous vide de gros morceaux de pneus a été démontrée. La faisabilité du procédé paraît avantageuse, avec des retours sur l'investissement de 31% après trois années d'opération.

INTRODUCTION

Tire recycling has become a necessity because of the accumulation of discarded tires which are a potential environmental risk. Each year 24 million tires (220 Gg) are disposed of in Canada and about 250 millions tires (2.3 Tg) in the U.S. Table 1 reports estimates of used tire arisings for the Economic European Communities and other countries. While some of these tires are recapped or ground for special uses, most are dumped in rural areas or in landfills. When buried in landfills, they eventually float to the surface. In piles, the non-biodegradable rubber can cause serious harm if ignited. Tires infested with mosquitos is a subject of increasing concern [3].

Table 1. Total Arisings of Used Tires in Different Countries

Country	Mg/Year	Reference
EEC	1 500 000	[1]
USA	2 300 000	[2]
JAPAN	579 000	[1]
CANADA	220 000	[2]

Tires represent a source of energy and chemicals. By thermal decomposition, it is possible to recover useful products. There have been numerous attempts to pyrolyze tires. It is beyond the scope of this paper to describe the various ventures and adaptations of technology. Literature reviews have been published [1, 4-6].

There appears to be only a few scrap tire commercial pyrolysis plants in the world, most of which operate in Japan (see Table 2). Of these, three operate on a continuous feed and one batch. Typical yields from the Kobe plant are 31% oil, 29% carbon black, 15% gas, 10% steel, 5% sludge and 2% water (8% loss in material

balance). The oil is sold to a cement kiln company. The economics of the plant was reported to be marginal [1].

Table 2. Existing Commercial Scrap Tire Pyrolysis Plants

Process or Company	Capacity	Location	Start-up Date
Hyben Recycler	Batch	Britain and Japan	1977
Kobe Steel	1 Mg/h	Aioi, Japan	1978
Onahama Smelting and Refining	4 Mg/h	Iwaki, Japan	1981
Kleenair	1 Mg/h	Centralia, Wash.	1986 (now closed)

The Kleenair process was developed by Conrad Industries in 1986 for the recycling of used rubber to gas, oil and carbon black. The plant capacity was 1000 kg/h, similar to the Kobe plant. In both cases, the feedstock consisted of shredded tires. The plant is not operating.

The distinct feature of the Onahama plant is that whole tires are used as feedstock to the reactor. The major saleable products are a heating oil (25-30%), carbon black (35-40%) and steel (10%). The carbon black is used in an adjacent copper smelting plant [7]. The economics of the process is good, although it has been reported to be less profitable than burning the tires at the plant site.

Some of the conclusions reached after visiting these plants are:

- The most successful recycling process is the one that uses whole tires as feedstock. Shredding tires is expensive and results in materials which are difficult to handle inside the reactor, eventually giving rise to the so-called "ballmilling" problem.
- The quality of the carbon black product greatly determines its end-use and as a consequence, its value.

- The plant operation should be supported by a high-quality control laboratory that should be operated by low-level technicians. In addition, the company should maintain a strong R and D activity for product improvement and development of new markets. None of the plants visited afforded such technical support.
- The process is cost sensitive to the supply of rubber feedstock. The process will be more profitable if there is a tipping fee or management cost attached to the reception of a tire.
- Attempts should be made to replicate the plants elsewhere near large piles through licence or franchise agreements in order to share the risk and optimize the investment.

VACUUM PYROLYSIS PROCESS

Vacuum pyrolysis is an old concept. It enables the production of large quantities of pyrolysis oils from organic substances. Vacuum minimizes secondary reactions such as thermal cracking, repolymerization and recondensation reactions, gas phase collision, catalytic cracking and reduction and oxidation reactions. If the vapor phase products are quenched, the yield of organic liquids such as pyrolysis oils is increased at the expense of solid residues and gases. The physicochemical properties of the end products are specific.

BACKGROUND

Laboratory tests were performed in a bench scale reactor to study the influence of temperature and particle size during pyrolysis. For these tests approximately 1 kg of feedstock was poured into the reactor vessel. Pressure was maintained below 3 kPa abs. during the run. The experiment was stopped when the final desired rubber bed temperature was reached. A detailed description of the apparatus and procedure used was reported [6]. Regular tires with no steel belt were used for this series of runs. The tires had been previously shredded to 1/4" - 1/2" Tyler sieves (6.35-12.70 mm). The chemical composition of the rubber feedstock is given in Table 3.

Table 3. Chemical composition of scrap tires used as feedstock

Elemental Composition	Proximate Analysis	Gross Calorific Value
81.5% C	65.2% Volatile matter	36.8 MJ/kg
7.1% H	28.7% Fixed C	
3.4% O	6.1% Ash	
0.5% N	(Moisture 0.5%)	
1.4% S		
6.1% ash		

The yields of oil and water, carbon black and gas produced during pyrolysis at varying final temperatures are presented in Fig. 1. The temperature shown is that of the bed of shredded tires. The maximum yield of liquids was reached at a plateau temperature of about 415°C; the yield of condensable products on a rubber as-received basis was 60.7%, of which 93% was pyrolysis oil.

The gas phase was mainly composed of H_2 , CO, CO_2 and a few hydrocarbons, as illustrated in Fig. 2. At 415°C, the gas had a gross calorific value of 37 MJ/kg with an average molecular weight of 28.3 Daltons. No H_2S could be detected in the gas phase. If any, its concentration must be low since a partial mass balance for sulfur gave 70.4% for the solid residue and 27.4% in the oil, leaving 2.2% for losses and gases.

Two runs were conducted at identical temperature ($420 \pm 5^\circ C$), one with pieces of rubber sieved between 6.4 and 12.7 mm, and the other with 150 to 400 mm. There was no significant difference between the two runs for the product yields (see Table 4).

Table 4. Influence of particle size on the product yields during vacuum pyrolysis of used tires at 420°C (wt. %, rubber as-received basis)

Size (mm)	Oil (%)	Carbon black and fibers (%)	Gas (%)	Water (%)
6.4 - 12.7	56.6	36.6	2.2	4.6
150 - 400	58.4	34.8	2.1	4.7

Similarly, vacuum pyrolysis at 450°C of a steel belt (17.6% fiber + steel) tire sample yielded 59.0% oil, 33.8% carbon black, 5.2% gas and 2.0% water on an organic rubber basis, in accordance with the results in Table 4.

In general, the mass balance for this series of runs reached 99.5%.

PROCESS DEVELOPMENT UNIT STUDY

These preliminary results were further investigated using a vacuum pyrolysis Process Development Unit (P.D.U.). The system operated on a semi-continuous feed mode using shredded regular used tire material sieved to 6.4- 12.7 mm mesh size. The reactor was a six hearth furnace, 2 m in height and 0.7 m in diameter. It was externally heated by electric elements surrounding the reactor chamber. The maximum throughput reached was 13 kg/h. A schematic of the P.D.U. is shown in Fig. 3. and a detailed description will be found elsewhere [6].

At a rubber bed temperature of 513°C, the product yields were 54% oil, 37.8% carbon black and fiber, 4.2% gas and 4.0% water. The mass balance typically closed at 96%. These results correlate with the bench scale data.

An important engineering parameter to be considered when designing a full scale pyrolysis plant is the quantity of energy required for the pyrolysis reactions. This has been empirically determined using the P.D.U.; and the detailed procedure has been published elsewhere [6].

The quantity of heat required to decompose rubber (H_r) will depend on the operating conditions used and the extent of reaction reached. Under normal carbonization conditions, the reactions are exothermic. Under vacuum, the reactions were found to be slightly endothermic, 700 kJ/kg. It was concluded that the secondary reactions (e.g., thermal and catalytic cracking, repolymerisation, recondensation, oxidation and reduction reactions), which occurred under normal carbonization conditions (higher pressure), released heat and hence contributed to the overall exotherm. The net overall thermal efficiency of vacuum pyrolysis is high, over 90% [6].

PILOT PLANT STUDY

The next step involved a further scale up of the P.D.U. to pilot plant scale. A sliding blade horizontal reactor was used instead of a multiple hearth furnace. The system was designed to continuously decompose 200 kg/h of steel belt tires at a pressure below 1.3 kPa. Large pieces of rubber were continuously fed across a column of water which connected a tank on the ground and the top of a horizontal reactor which was elevated 14 m in the air (see Fig. 4 and Photog. I). The reactor was externally fired with gas and a small portion of the pyrolysis oil. The vapors were quenched by two scrubbers set in series. The carbon black was recovered at the bottom of another water head which connected the bottom of the reactor and the ground. A sharp separation of the fiber, steel and carbon black was made in the water phase. The process schematic is given in Fig. 5.

The objective of the pilot plant study was to demonstrate the feasibility of the vacuum pyrolysis process using semi-industrial scale equipment under continuous operation over several hours. The reactor configuration and the reliability of the downstream equipment, including the scrubbers, gas cleaning system and pumps, were tested. The results obtained are:

- Continuous feeding of tires *in vacuo* was practicable.
- Separation of steel, fiber and carbon black at the reactor outlet is feasible.
- The equipment designed for the condensation and recovery of the pyrolysis oils well performed.
- The overall thermal efficiency of the process is good.

- The optimum temperature and pressure conditions to produce large yields of oils have been found.
- The three major products, oil, carbon black and steel, are saleable and marketable.
- No major problem is expected with the control of emissions.

The main limitation with this system was the low rate of heat transferred to the rubber per unit area of reactor surface. The reactor operated at less than half of its throughput capacity due to inefficient heat exchange in the chamber. Another improvement in progress is a better system for handling the rubber material inside the reactor by using large rubber (quarters) pieces as feedstock.

The pilot plant unit was built and tested during fall 1987 in Saint-Amable near Montreal. Unfortunately, the project was momentarily stopped during early 1988 because of the bankruptcy of the licensed company (Petro-Sun International, Inc.) due to facts unrelated to this project. With the financial support of both Université Laval and Energy, Mines and Resources Canada (Bioenergy Development Program), the project was continued at the P.D.U. level until now.

OIL AND CARBON BLACK ANALYSIS

The two main products obtained from the pyrolysis of tires are carbon black and oil. Samples of each obtained in the pilot plant unit were tested in this laboratory and by different customers. Some of the analytical results are reported below.

The oil has a gross heating value of about 43 MJ/kg, a specific gravity of 0.95 (17.8°API), a pour point of -6°C, initial boiling point 112°C with a 50% cut at 376°C (simulated distillation). The residual metal content is < 0.1% for Va, 0.1% for Ni and 0.6% for Na. A typical elemental analysis for the oil was 87.3% C, 10.5% H, 0.8% S, 1.2% O and 0.2% N. It yielded on distillation 8% of heavy naphtha, 16% kerosene, 24% light gas oil, 35% cat. feed and 17% bunker (vol.%). The PONA analysis of the fraction boiling below 204°C which constituted 26.8% of

the crude oils gave 24.9% Paraffins, 43.3% Olefins, 6.6% Naphthenes and 25.4% Aromatics. A detailed chemical analysis of some valuable compounds which are present in the pyrolysis oil has been made and is available in Appendice A of this report.

This oil can be used as a heating oil and would be grossly classified as a number 4 ASTM bunker oil. Alternatively, it can be refined as a crude oil and has several other potential applications under development. Table 5 is a partial list of the major compounds which have been detected [8]. These compounds have a potential value as petrochemical feedstock.

Table 5. Examples of compounds found in vacuum pyrolysis oils

Compound	Yield
(wt. %, as-received rubber basis)	
Limonene-ld	2.26
Toluene	1.05
o-,m-,p-Xylene	0.93
Styrene	0.82
Benzene	0.38
4-Vinyl-1-cyclohexene	0.25
Dimethylcyclopentadiene	0.24
Methylpentene	0.23
2,4,4-Trimethyl-1-pentene	0.22
α -Methylstyrene	0.19
Dimethylpentane	0.16
Cyclopentanone	0.15
Isopropylbenzene	0.15
Ethylhexadiene	0.13
Trimethylpentadiene	0.07
Methylhexadiene	0.06
3-Methyl-1,4-hexadiene	0.06

Table 6 summarizes some of the main characteristics of a representative carbon black samples produced under vacuum at 525°C. Carbon black samples produced during the pilot plant operation were shipped to two rubber product manufacturers. Both concluded that this carbon could partially replace commercial blacks for the preparation of low grade rubber parts. One manufacturer concluded that this material could be used as a substitute up to 20-40% of N-990 in a particular application. The other found that the recycled black has the potential to partially substitute for the N-774 commercial grade. At this stage of the research, carbon blacks derived from used tires contain several impurities. It is doubtful that there exists a short term market for this product in the tire industry. Work is progressing to purify the material in order to increase its ultimate quality. This recycled carbon has numerous potential uses including reinforcement or semi-reinforcement for bicycle tires, shoes, auto flaps, footwear, conveyor belts, dock fenders. Other uses also include pigments for ink and reduction for ore refining.

Table 6. General properties of a carbon black sample produced during vacuum pyrolysis of used tires

Iodine index (mg/g)	144.2 - 151.4
DPB absorption (mL/100 g)	84.6 - 93.0
Heat loss at 105°C (%)	0.4 - 1.0
Tint strength	57.1 - 60.6
Ash (%)	15.5 - 17.0
Volatile Matter (%)	4.9 - 3.3
S (%)	2.5 - 3.0

Ultimate temperature was 525°C and total pressure varied between 1.5 and 4.5 kPa. Feedstock included both regular and steel belt used tire samples.

PROCESS FEASIBILITY

Based on the data reported, a preliminary feasibility study of the process was performed. The assumptions used are summarized in Table 7. The "improved grade" for the oil and carbon black means that the market value for those products will increase due to further upgrading. The price of 220\$/tonne for year three for carbon black represents 40% of today's price for the bottom line blacks from major producers. The assumed tipping fee of 1\$/tire fits inside the current range of fees charged to dispose of tires near large North American cities. More and more states and provinces are enacting or considering legislation to clean up tire piles, which seems to be necessary to prevent speculation when there will be a market for tire recycling [9].

Table 7. Assumptions used for the process feasibility study

Product	Yield	Price
Oil	55%	Regular grade: 16 ¢/kg Improved grade: 18 ¢/kg
Carbon black	25%	Regular grade: 100 \$/Mg Improved grade: 220 \$/Mg
Steel	9%	120 \$/Mg
Fiber/Kevlar	5%	2 \$/Mg
Gas	6%	Used for make-up heat

Prices are in Can. \$.

Other assumptions:

Tipping fee	1 \$/tire
Tires per ton	110
Rate of inflation	5%/year
Re-usable tires	2% of tires @ 6 \$/unit
Re-caps	10% of tires @ 2 \$/unit

Table 8 shows that the profitability of a 3 metric tonnes per hour or 20 000 metric tonnes per year, with a capital investment of 7 M Can \$, is attractive if a tipping fee can be collected for recycling tires. The return on invested capital shown in Table 8 represents the invested capital valued at net book value of assets.

Table 8. Profitability of a 20 000 Mg/year plant for vacuum pyrolysis of used tires

Sales/Revenues (Can. \$)			
	Year 1	Year 2	Year 3
Oil, regular	645 000	1 354 000	
improved			1 422 000
Carbon black, regular	220 000	462 000	
improved			968 000
Steel	95 000	200 000	210 000
Fiber	1 000	2 000	2 000
Tipping fees/Cleanup	1 100 000	2 200 000	2 200 000
Re-usable tire	132 000	277 000	291 000
Re-caps	220 000	462 000	485 000
Total Sales/Revenues	2 430 000	4 957 000	5 578 000
Cost of sales	651 000	1 509 000	1 657 000
Gross margin	1 779 000	3 448 000	3 921 000
Adm. and comm. expenses	177 000	263 000	287 000
Depreciation	675 000	675 000	675 000
Financial expenses	473 000	473 000	473 000
Taxes	145 000	785 000	964 000
Profits (loss) of the year	309 000	1 252 000	1 522 000
Undivided profits (deficit) at the commencement	NIL	309 000	1 561 000
Undivided profits (deficit) at the end	309 000	1 561 000	3 083 000
Return on invested capital	5%	22%	31%

ENVIRONMENTAL ASPECTS

An assessment of the quality of the aqueous and gaseous pyrolysis effluents from an environmental point of view was performed. The investigation was made using the P.D.U. at a feed rate of 29 kg/h of cross-ply tires. The reactor temperature reached 550 °C at a total pressure of 10 kPa.

The noncondensable pyrolysis gases were burned in a Roberts Gordon burner (73 kW capacity) and the stack gases were sampled to determine the contaminants present in the effluent (run D015). SO₂ was measured following Environment Canada method EPS-1-AP-74-3 and varied between 74 and 219 ppm (v/v), 3 h and 10 h after the beginning of the experiment, respectively. CO was analysed with Dräger tubes; its concentration was 5 ppm (v/v) after 5.8 h and 30 ppm at time 7 h. NO_x was determined following Env. Canada method EPS-1-AP-77-3 and gave a peak of 222 ppm (v/v) at time 2.9 h. Unburned hydrocarbons were detected by GC and gave 1850 ppm (v/v). Particles content was evaluated using Env. Canada method EPS-1-AP-74-1; their concentration reached 48 mg/Nm³. However because perfect isokinetic sampling was not achieved due to the size of the chimney used (laboratory scale) and because an entirely satisfactory steady state operation of the reactor was not reached, these results are only preliminary.

The gas emission results were analysed in terms of Quebec Ministry of Environment regulations for the quality of atmosphere (Q-2r.20, MENVIQ). A thorough inspection of the norm led us to the conclusion that all contaminants except NO_x were well below the specified concentrations. NO_x concentration was borderline with NO_x standard for much bigger burners having a capacity greater than 15 MW. It can be expected that a better cleaning of the gaseous emissions using a liquid ring vacuum pumping system with associated downstream gas scrubber (instead of a mechanical pump), will further improve the quality of the gas emissions and render the process completely acceptable from an environmental point of view.

The aqueous phase sample from run D-014 was subjected to a Microtox evaluation by the firm Technitrol Eco. Their report is included in Appendice B hereto. 100 ml of the oil sample was thoroughly mixed with 100 ml of water during 2 minutes. The liquid sample was left still for one hour. Two phases were obtained. 75 ml of the aqueous phase was taken and used for the Microtox assay following the Bureau de Normalisation du Québec #3600-205 Method. The aqueous extract was found to be highly toxic for the bacteria tested (*Photobacterium phosphoreum*). This as such should not however be a serious problem. First of all, the aqueous phase yield represents less than 2% by wt. of the as-received material. Second, the water will likely be burned on site after blending it with a portion of the pyrolysis oil which will be used to heat up the reactor.

Figure and Photograph Captions

Figure 1. Influence of Decomposition Temperature on Products Yields during Vacuum Pyrolysis of Used Tires.

Ordinate: Yields (wt. %, rubber as-received basis)

Abscissa: Temperature ($^{\circ}\text{C}$)

Figure 2. Influence of Decomposition Temperature on Gas Phase Composition (Upper figure: major components. Lower figure: minor components).

Ordinate: Weight fraction of total gas (%)

Abscissa: Temperature ($^{\circ}\text{C}$)

Figure 3. Schematic of the Vacuum Pyrolysis Process Development Unit

Figure 4. Schematic of the Saint-Amable Pilot Plant

- Legend:
- 1.Feed conveyor
 - 2.Vacuum reactor
 - 3.Cooling screw
 - 4.Discharge screw
 - 5.Crusher
 - 6.Vibratory screen
 - 7.Carbon black handling system
 - 8.Heavy oil quencher
 - 9.Light oil quencher
 - 10.Decanter
 - 11.Vacuum pump
 - 12.Flare stack
 - 13.Heavy oil storage
 - 14.Light oil storage
 - 15.Magnetic separator
 - 16.Steel recovery bin

Photograph I: Vacuum Pyrolysis Pilot Plant in Saint-Amable, Québec

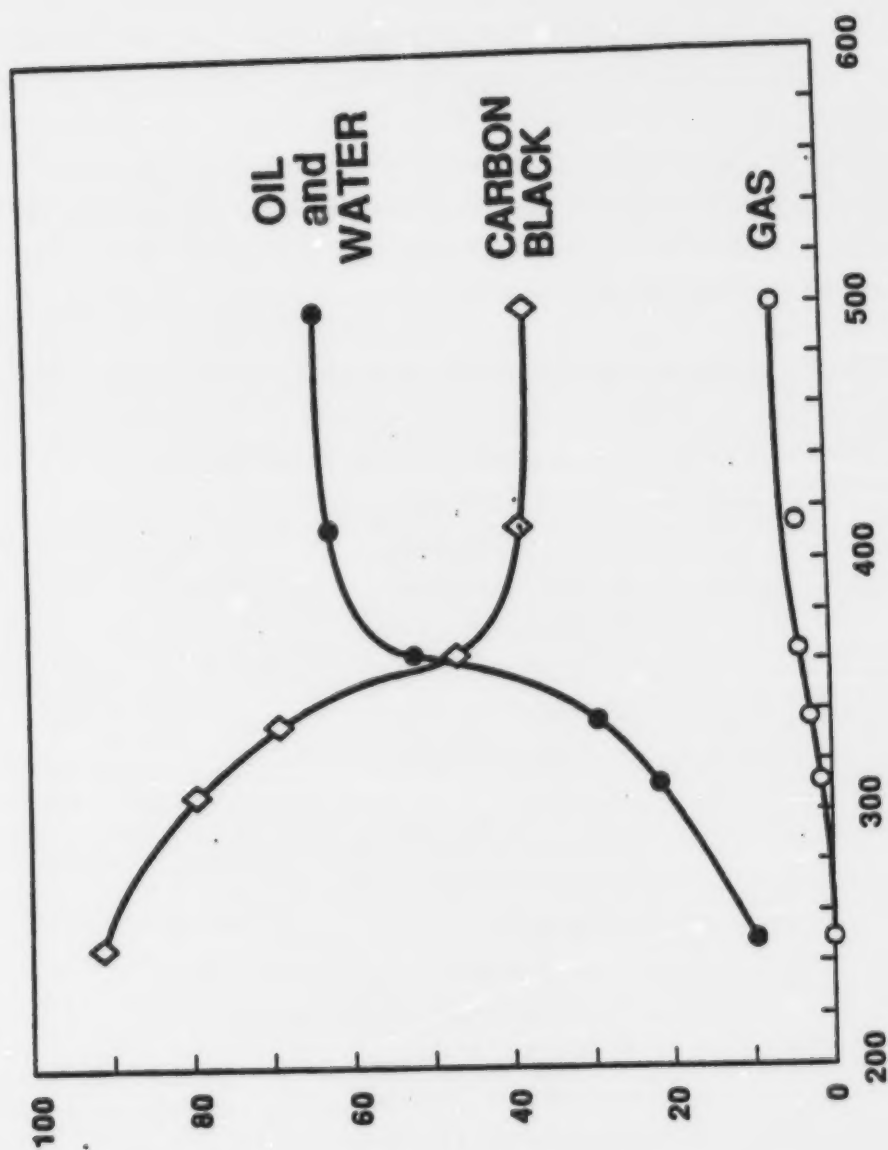


Figure 1. Influence of Decomposition Temperature on Products Yields during Vacuum Pyrolysis of Used Tires

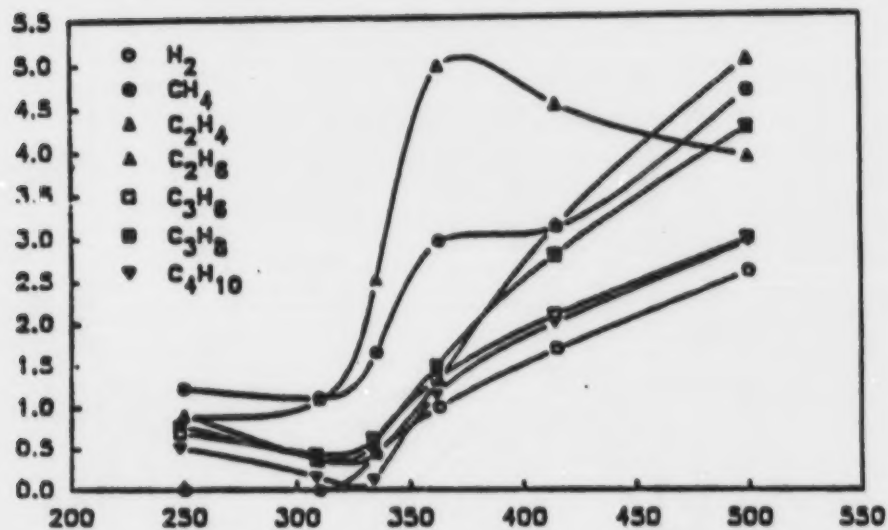
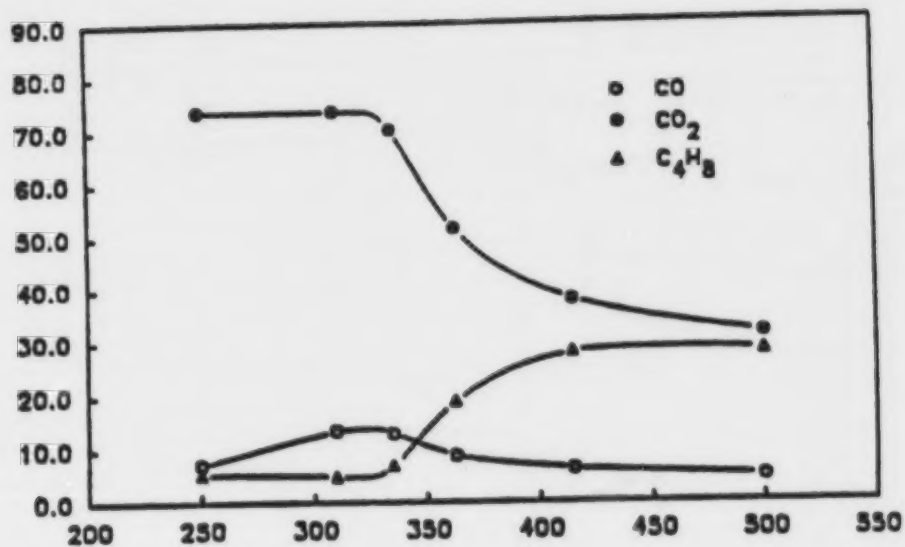


Figure 2: Influence of Decomposition Temperature on Gas Phase Composition

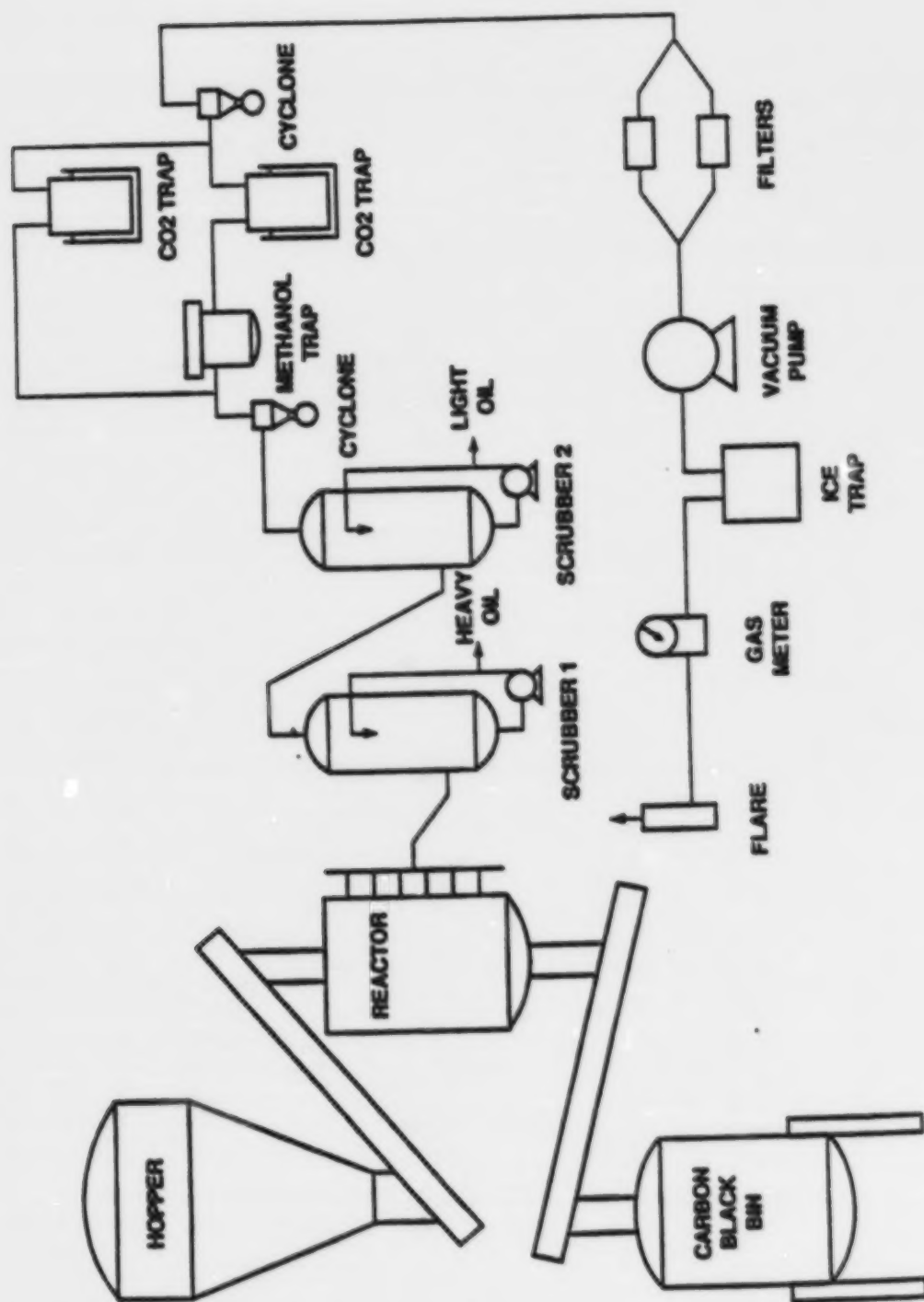
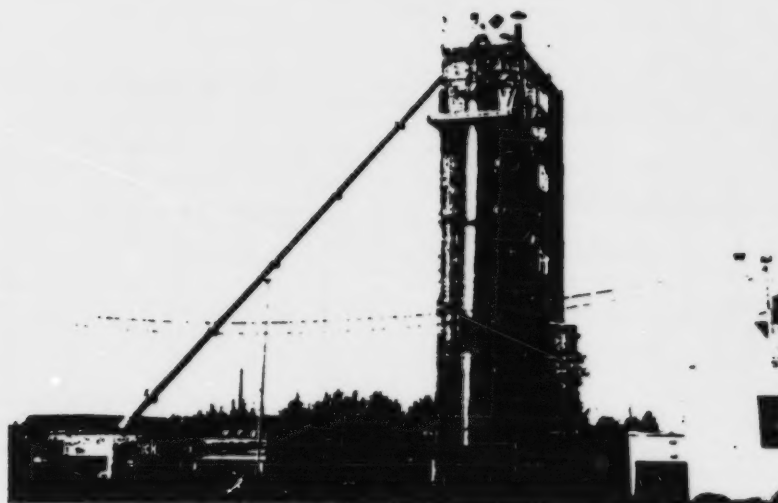


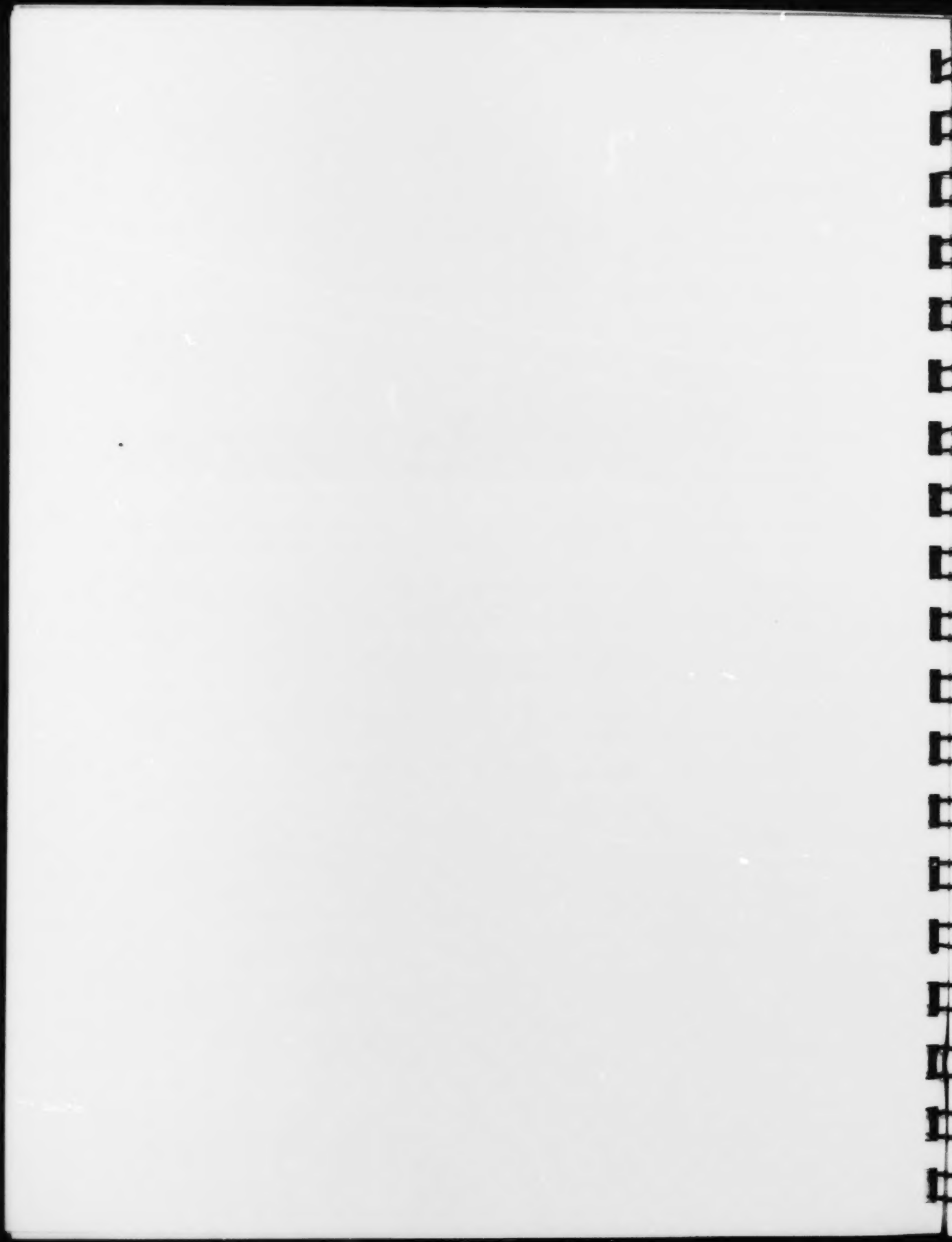
Figure 3. Schematic of the Vacuum Pyrolysis Process Development Unit.



Photograph I: Vacuum Pyrolysis Pilot Plant in Saint-Amable, Québec

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APPENDIX A

VALUABLE CHEMICALS FOUND IN
THE PYROLYSIS OIL



INTRODUCTION

Tire recycling has become an important environmental issue recently due to the huge piles of tires which represent a threat to the environment. There is about one worn tire produced per person per year in the developed countries(1).

Thermal decomposition of tire, a synthetic rubber, enables the recovery of carbon black and liquid hydrocarbon oil which have a potential economical value (1). Pyrolysis of tires under vacuum yields 55% (by wt.) oil, 25% carbon black, 9% steel, 5% fiber and 6% gas (2). The process has been tested in a 200 kg/h unit fed with steel belt tires at a total pressure of 1.3 kPa. The pyrolysis oil contains a significant portion of a volatile, naphtha-like fraction with an octane number similar to the petroleum naphtha. Its Benzene, Toluene and Xylene (BTX) content is also remarkably high. The naphtha fraction in addition, contains about 15% limonene, a terpene hydrocarbon. Potential applications of the pyrolysis oil (3) and carbon black (4) have been investigated. However, the process economics is greatly influenced by the quality of the oil and carbon black products (2).

This paper discusses limonene production during used tire vacuum pyrolysis with its postulated mechanism of formation. The limonene separation method from the the pyrolysis oil, as well as its purification and structural characterization are also discussed. Large scale limonene separation, purification and its feasibility study is under investigation.

Limonene is the chief constituent of citrus oil with over 80% and is mainly obtained by expression from the fresh peel of grapefruit, lemon, bitter and sweet orange at yields of 0.60%, 0.35%, 0.15% and 0.30% respectively. Limonene exists in two forms: d-limonene, the most naturally abundant, and dl-limonene (dipentene). Dipentene in addition is formed during the processing of sulfate liquor from kraft paper manufacture. Except for its optical activity, dipentene has the same physical properties as d-limonene.

Limonene has a fast growing and wide industrial application. It is used in formulation of industrial solvents, resins, adhesives and as a dispersing agent for pigment. It is also used as feedstock for the production of various kinds of terpenoid alcohol fragrances. L-Carvon for example, is synthesised from limonene and is used in the manufacture of synthetic spearmint flavoring in toothpastes and mouthwashes; its market spot price ranges between 20 and 25\$/kg (5). Originally, these alcohols were isolated from essential oils. During the past 20 years, development of the terpene alcohol chemistry and its application in perfumery has considerably increased and has led to the manufacture of olfactively high value products. The solvency of limonene and its swelling and softening properties make it useful for rubber reclaiming in the processing of natural and synthetic rubbers. It is sometimes used as diluent for pine oil in flotation applications (6).

The ever growing concern about the potential toxicity and environmental impact of conventional industrial cleaning solvents has been widely reported (7). This has stimulated interest in the use of limonene, a natural solvent, because of its pleasant nature, excellent solvency, rinseability and high wetting, penetrating and detergent properties. Limonene, a solvent and fragrance, is also biodegradable

and environmentally safe. It is not surprising that it has gained extension of its use into a wide range of applications including water-based degreases, natural lemon-scented all-purpose cleaners and lotion-like waterless hand cleaners. Limonene has been recently incorporated as the main ingredient of over one hundred household cleaning agents and industrial hand cleaners due to its environmental safety. Various chlorinated and fluorinated solvents, like the chlorofluorocarbons (CFCs) used in electronic circuit board cleaner formulation (180 M t/y worldwide), are now being partially replaced by limonene. Americal Telephone and Telegraph Company (A T & T) has currently substituted 1.5 Mkg of CFCs with limonene. All CFCs will be completely out of use before December 1999. The decision was made by the environment ministers of 59 nations plus the European Community on 29 June 1990 in London (7,8).

As a result, the demand for limonene has significantly increased over the last two years and prices are rising steadily. Limonene had a 50% growth demand over the 12 months to May 1989 (9). Worldwide demand for limonene in 1988 was about 27 000 t/y (10). Brazil, Florida and California to some extent, are the major limonene suppliers. Brazil and Florida produced about 600 and 800 tonnes of limonene respectively in 1987 (11). Citrus oil has received an increased interest during the last few years but its supply is severely limited to the seasonal upswing. Citrus oil supply tightens and market price fluctuates as the citrus season ends or when unfavorable crop raising conditions occur. It has been reported that the demand for citrus oils and their derivatives is growing faster than its supply so that no real balance is expected in the near future between the supply and demand (12). Limonene price was U.S. \$0.80/kg during 1987 which was up to U.S. \$1.6/kg during 1988. Limonene price varied between 2.4 and 3 U.S. \$ per kg during July 1989 (5).

EXPERIMENTAL

The pyrolysis oil samples were produced from used tires in a multiple hearth vacuum pyrolysis Process Development Unit (P.D.U.). The reactor was a six hearth furnace, 2 m height and 0.7 m in diameter. The system operated in a semi-continuous feed mode using shredded tires (1/4 inch to 1/2 inch). The reactor maximum temperature and total pressure were 510°C and 1 kPa respectively. The feeding rate was 3.5 kg/h. The PDU shown in Figure 1 has been described in details elsewhere (2). The organic vapors were removed from the reactor chamber by a mechanical vacuum pump and condensed in a series of condensers (H-1 to H-VI) installed in parallel at the reactor outlets corresponding to the six reactor hearths. The noncondensable gases from the Primary Condensing Unit (P.C.U.) were collected in a train of receivers (C-1 to C-4) which served as Secondary Condensing Unit (S.C.U.). The reactor hearth temperatures were stabilized at 227, 296, 366, 404, 450 and 510°C from top to bottom, respectively. That process yielded 55% by wt. oil during a typical run.

A prorata mixture of the pyrolysis oils from H-I to H-VI and C-1 to C-4 was prepared and distilled under atmospheric pressure up to 204°C to separate the naphtha fraction.

1 g of the distillate was fractionated over 20 g of impregnated silica-gel (10% Ag NO₃, 60 - 200 mesh). The first fraction was collected with 50 ml of n-pentane and followed by elution with 100 ml of 5% dichloromethane in n-pentane by collecting 5 ml fractions. All the fractions were analysed by GC. Limonene was identified with a purity of over 80%. The limonene fraction was further purified by then larger chromatography which resulted in 95% purity. The product was

further analysed on a Carl Zeiss 369414 polarimeter for its optical activity.

Gas chromatographic analysis was performed on a Varian 6000 chromatograph with 30 m X 0.25 mm i.d. DB-5 (J & W) capillary column and FID detector. The GC oven temperature was held at 35°C for 10 min, then increased to 100°C at 2°C min⁻¹ and to 290°C at 30°C min⁻¹.

Nicolet 60 SX FTIR spectrometer coupled to a Varian 6000 chromatograph was also used to characterize the total naphtha fraction.

RESULTS AND DISCUSSION

Gas chromatographic analysis of the pyrolysis oils obtained from the reactor hearths, H-1 to H-VI, as well as a naphtha fraction from a prorata oil were made. Unambiguous assignment of dipentene (limonene-ld, racemic form) was made by coinjection of an authentic dipentene (from Aldrich) and by GC/FTIR analysis. Polarimetric analysis of the purified limonene sample also confirmed its racemic structure. Dipentene contributed about 15% of the naphtha fraction or 2.2% by weight of the as-received tires.

Besides dipentene, benzene (25%), toluene (7.0%), xylene (6.1%) and styrene (5.4%) were the most abundant compounds in the pyrolysis oil. A few other compounds have also been identified which were not reported earlier in the literature (13-18): Vinyl-1-cyclohexene (1.7%), Dimethylcyclopentadiene (1.6%), Methylpentene (1.4%), 2,4,4-Trimethyl-1-pentene (1.4%), α -Methylstyrene (1.2%), Isopropylbenzene (1.0%), Dimethylpentane (1.0%), Ethylhexadiene (0.8%), Trimethylpentadiene (0.5%) and 3-Methyl-1,4-hexadiene (0.4%). The weight percentages are based on the distillate fraction boiling below 204°C at 1 atmosphere.

The naphtha yield represented 26.8% of the total pyrolysis oil. Its compositional analysis revealed a higher aromatic hydrocarbon content compared with the petroleum naphtha thus reflecting its higher octane number. It, however, suffers from high olefinic hydrocarbon content which is not a desirable fraction which can presumably be upgraded to a petroleum type naphtha. The pyrolysis naphtha had a gross calorific value of 43.7 MJ/kg, slightly lower than petroleum naphtha (46.0-47.0 MJ/kg) (19). Alternate usages of the other pyrolysis oil fractions are

currently under investigation in our laboratory.

GC analysis of the pyrolysis oil from H-I to H-VI revealed the presence of dipentene in H-II to H-V whereas only trace amounts were observed in H-VI oil fraction. Dipentene distribution in H-II to H-V produced at a temperature range of 250 to 440°C was found to be the most likely rubber degradation temperature range under vacuum for dipentene production. Similar to dipentene, 4-vinyl-1-cyclohexene was also identified in the naphtha fraction in a similar temperature range and contributed for 1.7% of the total pyrolysis naphtha fraction.

Tires are basically made of styrene and butadiene copolymer (SBR) or polybutadiene or a mixture of polybutadiene and polyisoprene. Thermal decomposition of natural rubber has been studied over the years under both atmospheric and subatmospheric pressure conditions and up to approximately 700°C. During the late twenties, Midgley and Henne (20) found that isoprene and dipentene were the predominating products of the destructive distillation of rubber. Degradation behavior of rubber is a function of the process conditions used, crosslinkage and how rubber is cured. Most of the thermal degradation studies of rubbers have been made under inert atmospheric conditions. A recent investigation by Tamura and coworkers reported that dien rubber undergoes thermal random scission along the main chain in vacuo or in an inert gas, producing polythiyl radicals (21). The polymer radicals produced at low temperature below 250°C will react by recombination, addition and disproportionation reactions in the solid-liquid phase. Various gaseous primary fragments including isoprene and butadiene monomers are produced at temperatures typically

between 250 and 450°C. As the reaction proceeds further, two isoprene or butadiene molecules formed in the initial stages will be rapidly converted to secondary products, i.e. 1-methyl-4-(1-methylethenyl)cyclohexene(dipentene) and 4-vinyl-1-cyclohexene by means of Diels-Alder reaction (Figure 2).

Dipentene and 4-vinyl-1-cyclohexene yields depend on the reaction temperature. Intermediate free radicals and dimers, dipentene for example, are also thermally unstable at higher temperature and reaction will proceed by recombination and further pyrolysis following dehydrogenation and reverse Diels-Alder reactions. Since we did not observe any significant amount of dipentene and 4-vinyl-1-cyclohexene in H-VI oil therefore it can be concluded that either dipentene formation ended below 440°C (hearth # 5 bed temperature) or decomposed simultaneously after formation at 510°C (hearth # 6 bed temperature).

Thermal reaction of 1,3-butadiene has been studied earlier at higher temperatures (550 to 750°C) (22). 4-vinyl-cyclohexene was the sole product below 600°C. As the reaction temperature was raised, cyclohexene, cyclohexadiene, benzene, butene, propylene, ethylene, methane and hydrogen were formed. C₆ cycloolefins are intermediate compounds. Their concentrations increased during the initial stage of the reaction, passed through maxima, and eventually were converted to the final aromatic products through reverse Diels-Alder and dehydrogenation reactions or both. Hydrogen and methane which are thermally stable, increased in amount as the reaction progressed.

An earlier report on pyrolysis of synthetic rubber at 350°C under atmospheric pressure of nitrogen similarly showed dipentene as the major initial product which was followed by disproportionation to the other derivatives such as methyl-isopropyl benzene under prolonged heating (23). In the same work, the authors observed that under certain conditions, dipentene, the expected major product, was no longer a significant component. Carbon black, sulfur and other metallic oxides tended to accelerate dipentene disproportionation reaction.

This could explain why dipentene has not been observed in tire pyrolysis oils obtained at temperatures above 500°C as described earlier in the literature. Vacuum apparently accelerated removal of various unstable gas and vapor molecules from the hot chamber and reduced the secondary reactions.

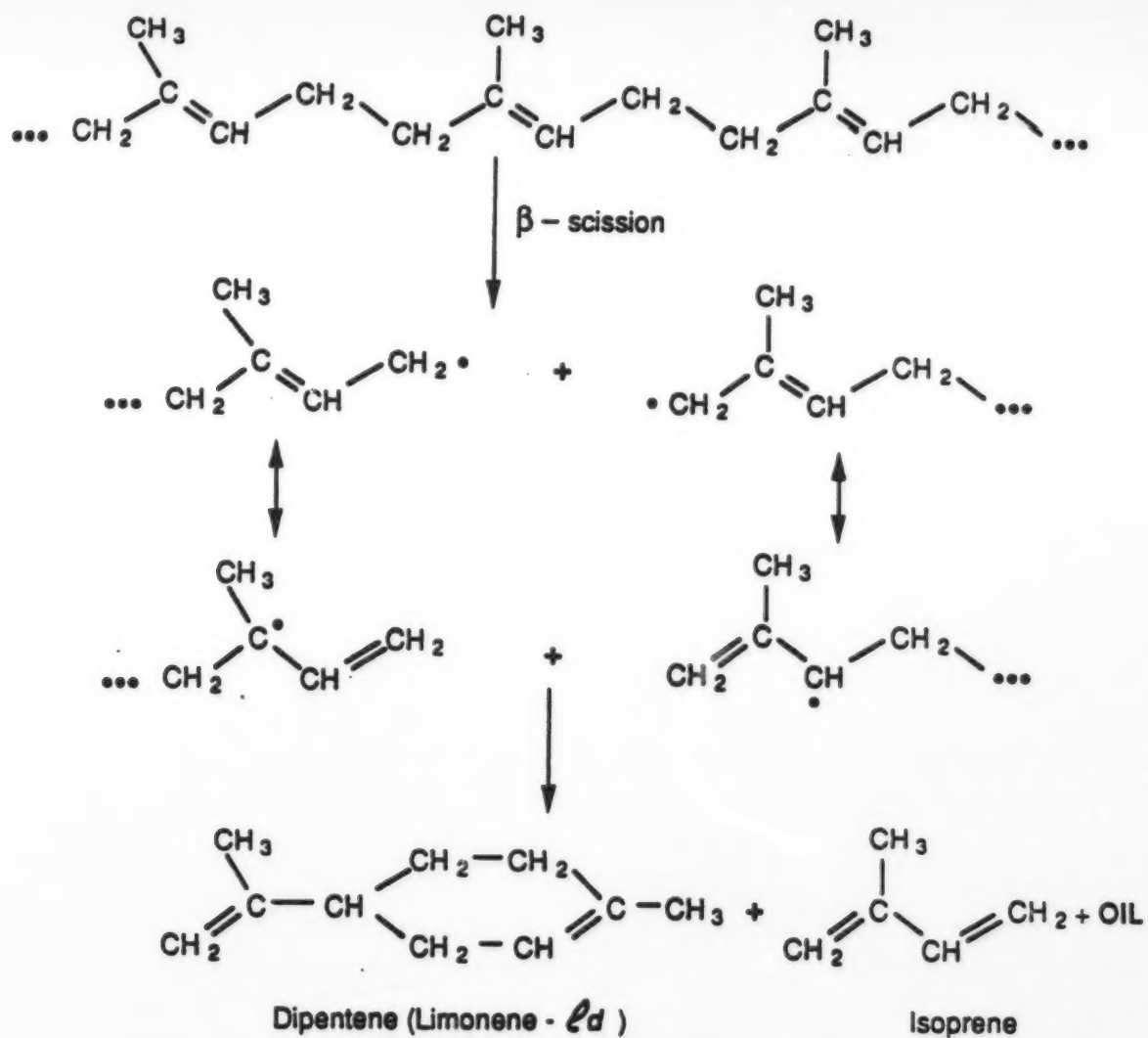
CONCLUSION

Process Development Unit vacuum pyrolysis of used tires, an increasing source of environmental and fire - hazard problems, yielded 55% by weight oil, 25% carbon black and 6% gas. The pyrolysis oil contains 26.8% naphtha. Compositional analysis of the naphtha revealed a higher aromatic hydrocarbon content such as benzene (2.5%), toluene (7.0%), xylene (6.1%) and styrene (5.4%), compared with the petroleum naphtha. Dipentene (dl-limonene) with a fast growing and wide industrial application contributed to 15% of the naphtha which was produced under vacuum and temperature range of 200 to 450°C. Higher tire decomposition temperature and prolonged heating results in decomposition and dehydrogenation of dipentene.

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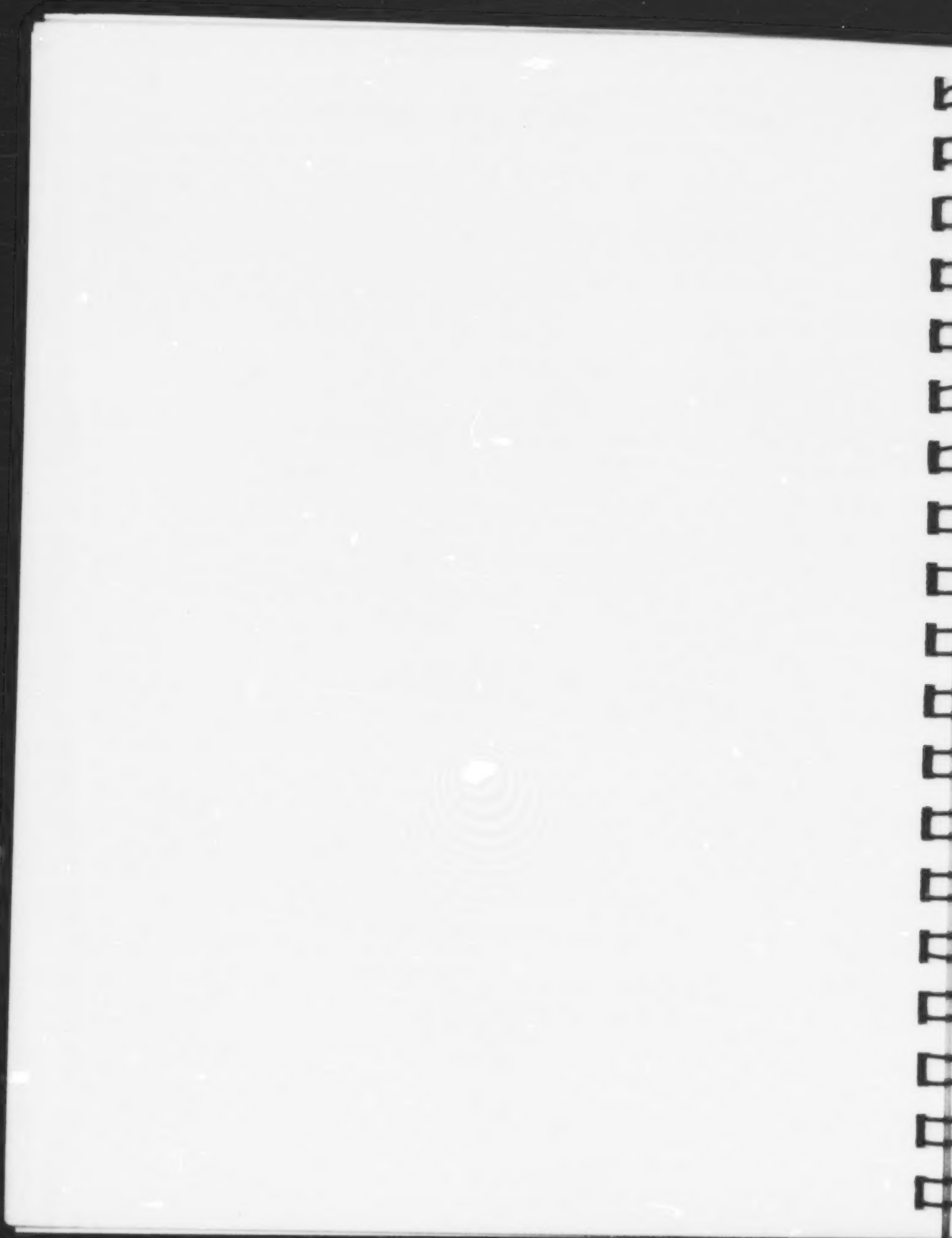
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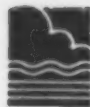




APPENDIX B

MICROTOX TESTING OF THE AQUEOUS PHASE





TECHNITROL-ECO
RECHERCHES • RESEARCH

45

Pointe-Claire, le 31 août 1990

Monsieur Christian Roy
Président
RECHERCHE CARBOVAC INC.
1560, avenue du Parc Beauvoir
SILLERY (Québec)
G1T 2M4

Notre numéro de projet: 905479

Monsieur Roy,

Il nous fait plaisir de vous transmettre les résultats de l'essai Microtox exécuté sur votre échantillon d'huile de pyrolyse D-014.

Ne pouvant effectuer l'essai directement sur l'échantillon d'huile, nous avons préalablement procédé à une extraction en milieu aqueux.

À cet effet, 100 ml de l'échantillon ont été placés dans une ampoule à extraction de 500 ml avec 100 ml d'eau utilisée dans nos laboratoires pour l'élevage des truites.

Après une agitation vigoureuse de 2 minutes, une période de repos d'une heure a été nécessaire à la séparation des phases.

905479

/2

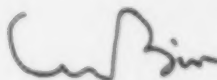
Cette période terminée, approximativement 75 ml de l'extrait aqueux (phase la plus dense) ont été prélevés et immédiatement soumis à l'essai Microtox.

Cet essai a été exécuté selon le protocole normalisé du Bureau de Normalisation du Québec dont une brève description est présentée ci-après.

Vous trouverez aux tableaux ci-joints, les résultats obtenus lors de ces tests.

Nous espérons que le tout sera à votre satisfaction. Si vous avez des questions relatives à ce rapport, n'hésitez pas à communiquer avec nous.

Recevez, Monsieur Roy, l'expression de nos sentiments les meilleurs.



Yves Bois, agr. M.Sc.
Superviseur du laboratoire
d'Écotoxicologie

YB/sc

p.j.

TESTS DE TOXICITÉ AVEC BACTÉRIES

Principe

A l'aide de l'appareil Microtox, l'inhibition de l'activité bioluminescente de la bactérie marine *Photobacterium phosphoreum* est déterminée.

Matériel biologique

Le réactif Microtox est utilisé. Il consiste en une souche génétiquement uniformisée de la bactérie; ces cultures sont conservées lyophilisées jusqu'au moment du test.

Mode opératoire

La méthode utilisée est celle adoptée par le Bureau de Normalisation du Québec (BNQ, # 3600-205) et peut se résumer comme suit:

Nous utilisons l'appareil Microtox (Modèle 2055, Toxicity Analyser System, Beckman Instruments Inc.). Cet instrument photométrique de précision est conçu spécifiquement pour le réactif Microtox. Le mécanisme lumineux de la bactérie étant intimement lié aux divers processus métaboliques cellulaires, une agression toxique aura donc, généralement, pour effet de diminuer son activité lumineuse. Le test est réalisé à au moins cinq concentrations; on détermine ensuite la concentration occasionnant une réduction de 50% de l'intensité lumineuse normalement produite par le réactif bactérien suite à une incubation de 5 et/ou 15 minutes à 15°C (CI50-5 et/ou 15 minutes, 15°C). Au besoin, un test de couleur est préalablement effectué. Il permet de compenser pour l'absorption lumineuse que pourrait provoquer la turbidité ou la coloration du produit. La compilation des résultats est réalisée par ordinateur à l'aide d'un programme mis au point par la compagnie Beckman et modifié par Environnement Canada (Longueuil).

**TECHNITROL-ECO**
RECHERCHES • RESEARCH

121 Boul. Hymus, Pointe Claire, Québec H9R 1E6 Tél.: (514) 697-3273 Fax: (514) 697-2090

RECHERCHE CARBÓVAC INC.
1560, avenue du Parc Beauvoir
SILLERY (Québec)
G1T 2M4

Le 31 août 1990

de projet: 905479
de client: 2765À l'attention de Monsieur Christian Roy**RÉSULTATS • RESULTS**

IDENTIFICATION DE L'ECHANTILLON	NUMERO DE TEST	DATE DE RECEPTION	DATE D'ANALYSE	CI 50 - 5 MINUTES % v/v (Int. Conf. 95%) <i>P. phosphoreum</i> (Microtox)
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EXTRAIT AQUEUX DE
L'ECHANTILLON D-014

2518

26/07/90

24/08/90

0.064 (0.045-0.090)

SOMMAIRE DES RESULTATS:

L'extrait aqueux a démontré de la toxicité aiguë pour les bactéries. Aux fortes concentrations, la toxicité est probablement due au pH élevé de l'échantillon (pH > 12). A 0.5 % (V/V) le pH de la solution est entre 6 et 7 et n'est donc pas responsable de la toxicité observée.

L'eau utilisée pour la préparation de l'extrait a démontré aucune toxicité pour les bactéries.

Int. Conf. : Intervalle de Confiance à 95%

Martine Drolet

Technicienne en Environnement
Département Ecotoxicologie

CE RAPPORT EST POUR L'USAGE EXCLUSIF DU CLIENT ET NE PEUT ÊTRE REPRODUIT SANS UNE PERMISSION ÉCRITE DE TECHNITROL-ECO INC. LES ÉCHANTILLONS MENTIONNÉS PLUS HAUT SERONT CONSERVÉS PENDANT 30 JOURS À PARTIR DE LA DATE DU RAPPORT À MOINS D'INSTRUCTIONS ÉCRITES DU CLIENT.
THIS REPORT IS FOR THE EXCLUSIVE USE OF THE CLIENT AND MAY ONLY BE REPRODUCED BY WRITTEN PERMISSION FROM TECHNITROL-ECO INC. UNLESS OTHERWISE INSTRUCTED ANY SAMPLE PERTAINING TO THIS REPORT WILL BE KEPT 30 DAYS AFTER REPORT DATE.

CONDITIONS D'ANALYSES

Description de l'échantillon:	Extrait aqueux de l'échantillon D-014
Date d'analyse:	24/08/90
Notre numéro de projet:	905479
Notre numéro de test:	2518
Organismes:	<i>Photobacterium phosphoreum</i>
Numéro de la culture:	M - 910
pH de l'échantillon (100% v/v):	>12
Préparation de l'échantillon:	Salinité ajustée à 2‰ avec du NaCl

[illegible]

* : calculé après avoir effectué les corrections applicables.